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(54) A process for preparing a microporous membrane and such a membrane.

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 DATABASE WPIL, AN 88-202856, Derwent Publication, London, GB; & CHEMICAL ABSTRACTS, vol. 109, no. 18, 31st October 1988, page 75, abstract no. 151087d; SASAKI JUN et al.: "Preparation of microporous polysulphone membranes"

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PATENT ABSTRACTS OF JAPAN, vol. 12, no. 338 (C-527)[3185], 12th September 1988, page 30 C 527; & JP-A-6397202 (TORAY IND. INC.) 27-04-1988; & DATABASE WPIL, Derwent Publ. London, GB, AN 88.157690

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Description

This invention relates to a process for preparing a microporous membrane, starting from a hydrophobic polymer and a hydrophilic polymer, by dissolving these polymers first in a solvent or a mixture of solvents and, subsequently coagulating the dissolved polymers in a coagulation bath, and subjecting said membrane to a heat treatment as well as to such microporous membranes.

Such a process has been disclosed in EP-A-0261734. The just-mentioned application describes a process for preparing hydrophilic porous membranes based on a mixture of at least two polymers, i.e., a hydrophobic polymer (preferably a polyetherimide) and a hydrophilic polymer (preferably polyvinylpyrrolidone). An essential aspect of the known process is based on the fact that the hydrophilic polymer, still present after coagulation, will be cross-linked in an unswollen state, in such a way that swelling will be limited to an acceptable minimum, while the thus obtained membranes can be used for filtration applications. The permeability of these membranes is in accordance with the pore size and the porosity which can be observed by means of e.g., an electron microscope. The above-mentioned cross-linking of the hydrophilic polymer preferably takes place by means of a suitable heat treatment, but the cross-linking can also be effected chemically.

It is noted that the cross-linking of the membranes is absolutely necessary, because otherwise the hydrophilic polymer present, preferably polyvinylpyrrolidone, swells too much, resulting in only very poor permeability values.

A special aspect of the invention described in EP-A-0261734 is the fact that a considerable amount of hydrophilic polymer, especially polyvinylpyrrolidone, remains in or on the membrane matrix after coagulation in a water bath or generally in a bath comprising a solvent (but a non-solvent for the hydrophobic polymer) for the hydrophilic polymer. It also appeared that the hydrophilic polymer present in the polymer solution partly remains in the matrix and is thus also partly found in the coagulation bath. This and that can be demonstrated by a method, which has been especially developed for measuring the concentration of the hydrophilic polymer in the coagulation bath.

Besides the advantages described EP-A-0261734 the known membranes have a number of disadvantages.

As an important disadvantage can be mentioned that cross-linking the remaining hydrophilic polymer may give rise to a relatively brittle membrane causing problems with the incorporation of the membranes in modules.

Further, the known membranes are always hydrophilic, which cannot always be considered an advantage.

Finally, the amount of hydrophilic polymer in the matrix is hard to control.

JP-A-61 238 834 discloses a multi-porous film of polysulphone-based resin containing a hydrophilic polymer e.g. polyvinyl pyrrolidone.

JP-A-63 141 610 teaches the production of a microporous membrane by flow-extending soln. of containing polysulphone and polyvinylpyrrolidone on carrier and dipping in coagulating bath.

JP-A-63 97 202 discloses polyether sulphone for semipermeable membrane - contains hydrophilic polymer component e.g. PVP for heat and chemical resistance.

The present invention now aims at providing a process, which solves the above-mentioned disadvantages in an effective way.

To this end the present invention provides a process for preparing a microporous membrane, starting from a mixture of at least a hydrophobic polymer and a hydrophilic polymer, by dissolving these polymers first in a solvent or mixture of solvents and, subsequently coagulating the dissolved polymers in a coagulation bath, removing the membrane so obtained from the coagulation bath and subjecting said membrane to a heat treatment, characterized in that the membrane prior to the heat treatment is treated with an oxidising agent to leach at least a part of the hydrophilic polymer from the matrix.

Detailed features of this process are delineated in claims 2-7.

Claim 8 concerns the membranes resulting from the process according to claims 1-7 when the hydrophilic polymer is partly or substantially leached from the matrix.

Surprisingly, according to the present invention, it appeared to be possible to control the amount of hydrophilic polymer in the membrane matrix, in such a manner, that the amount of hydrophilic polymer in the membranes finally obtained can have a value of about 0-35% by weight, based on the total dry weight of polymer in the membranes.

According to the invention the hydrophilic polymer from the matrix can be removed partly or substantially, so that the hydrophilicity respectively the hydrophobicity of the membrane can be regulated according to necessity. In case that about all of the hydrophilic polymer is removed, the present invention provides the interesting possibility to prepare a very porous hydrophobic membrane matrix on the basis of a mixture of a hydrophilic and a hydrophobic polymer. It is noted that for obtaining a porous matrix it is necessary per se that use is made of a hydrophilic polymer with the followed

membrane preparation procedure. That is the application of the hydrophilic polymer is essential for obtaining a porous membrane structure, in which the pores are interconnected in an optimal manner, so that the membranes can be applied for filtration purposes in a suitable way.

An important aspect of the present invention can be found in the fact that the desired porous structure in the membranes can only be obtained when the membranes are subjected to a suitable post-treatment.

It appeared that in a number of cases the complete or incomplete removal of the hydrophilic polymer can be accomplished in a water bath, which absorbs much time and has further the disadvantage that the hydrophobic polymer present, e.g. polyetherimide, is affected by hydrolysis.

According to the present invention the removal/leaching of the hydrophilic polymer is realised by treatment of the membrane with an oxidising agent. Examples of these are acidified potassium permanganate ($KMnO_4$), hydrogen peroxide, sodium peroxide etc. etc.. Advantageously a sodium hypochlorite solution can be applied.

By applying a sodium hypochlorite solution leaching occurs considerably faster than in a water bath, whereby furthermore the remaining hydrophobic matrix is not at all or hardly affected.

Further, the treatment with sodium hypochlorite solution has the advantage, that the membranes so treated are very suitable as filtration membranes, because the swelling of the hydrophilic polymer still present is reduced in such a manner, that no clogging of the pores occurs. Owing to this the fluxes of the membranes so obtained are in accordance with the size of the pores and the porosity of the membranes, as can be observed by means of an electron microscope. It should be noted, that after the treatment of the membranes with sodium hypochlorite solution there is still sufficient hydrophilic polymer left behind to give the membrane a hydrophilic character which still allows wetting the membranes with water.

However this hydrophilicity or water wettability of the membranes according to the invention disappears when the membranes are subjected to treatment at elevated temperatures after the mentioned treatment with sodium hypochlorite solution. Therefore the membranes are heated to approximately $150^\circ C$ for 2-30 hours. The thus heat-treated membranes can be considered to be hydrophobic.

It is noted that, as hydrophobic polymer according to the invention preferably polyetherimide, polyethersulphone, polysulphone, polyimide, etc. and as hydrophilic polymer polyvinylpyrrolidone, polyacryl acids polyvinyl-alcohol, polyvinylacetate, polyethylene glycol etc. etc. are used.

As a solvent for the polymer according to the invention one uses in general N-methylpyrrolidone, dimethylformamide, dimethylacetamide, dimethylsulphoxide, chloroform, methylenechloride etc. etc..

5 For the preparation of the microporous membranes according to the invention hydrophobic polymer / hydrophilic polymer / solvent ratios of 10-35% by weight / 15-35% by weight / 85-30% by weight are generally used, and preferably 25-20% by weight / 10-15% by weight / 75-65% by weight.

It is noted that according to the invention flat membranes, tubular ones, either on or off a support, as well as in the form of hollow fibers can be prepared.

15 Finally, the invention also relates to microfiltration and/or ultrafiltration membranes, flat or tubular or in the form of hollow fibers, consisting essentially of a hydrophobic polymer and more or less of a hydrophilic polymer, which hydrophilic polymer has been cross-linked and fixated in or at the polymer matrix, the membrane having pores of 0.0001-5 μm , a heat resistance up to $250^\circ C$, a water permeability up to 8000 $l/m^2.h.bar$, also having a good chemical resistance and good mechanical strength.

It appeared that the membranes according to the invention are very suitable for membrane separations, based on particle sizes, e.g. ultra- and microfiltration. It is apparent that the present membranes are not to be restricted to the applications just cited. For example the hydrophobic embodiments of the present membranes can advantageously be used as aeration medium, oxygenator, bioreactor etc.. For special applications it is also possible to provide the capillary membranes with a hydrophobic (e.g. the inner surface) as well as a hydrophilic surface (e.g. the outer surface).

40 The degree of hydrophilicity is especially of interest in connection with protein adsorption or in a general sense in connection with the so called fouling of membranes. Until today there is little agreement in the literature concerning a good relationship between the degree of hydrophilicity and the fouling properties of membranes, while the plurality of the knowledge in this field is based on experimental results. It appeared from research by Applicants that the adsorption of BSA (bovine serum albumine, a model protein, which is often used for fouling studies) on membrane surfaces depends 45 on the post-treatment of the membranes. The amounts of adsorbed BSA to PEI/PVP membranes, which have been subjected to a heat treatment (see Example I), is approximately $2 mg/m^2$ membrane surface and is comparable with the amounts for cellulose type membranes presented in the literature. This latter type of membrane is still considered to be the best example for non-fouling membranes. If the PEI/PVP membranes are sub-

jected to a NaOCl treatment (see Example II) or a NaOCl treatment followed by a heat treatment (see Example III), then the amount of adsorbed BSA is approximately 8 mg/m₂ membrane surface. It is remarkable that hardly any difference can be detected in the amount of BSA adsorbed between the membrane of Example II (hydrophilic) and the membrane of Example III (hydrophobic), which gives a good illustration of the fact that the degree of hydrophilicity plays an important role in fouling. It should be noted that it is conceivable that, in contrast, the membrane of Example II shows good anti-fouling properties if other feed solutions are used.

It may be obvious that the leaching process with e.g. sodium hypochlorite solution affords the possibility to control the hydrophilic character of the membranes and to adjust it to the desired conditions.

The invention will now be illustrated with the following not limitative examples.

EXAMPLE I

A solution was prepared from 17 parts by weight polyetherimide (Ultem® 1000), 13 parts by weight PVP in 70 parts by weight N-methyl-2-pyrrolidone. The thus obtained polymer solution was spun to a capillary membrane by coagulation in a water bath with a temperature of 20°C-80°C.

After removal from the coagulation bath the membranes were dewatered by subsequent treatment with ethanol and hexane. After deswelling the membranes were subjected to heat treatment at 150°C for 2-30 hours.

After this treatment the membranes still contained 20-25 parts by weight PVP based on the total membrane weight. The water flux of these membranes was 500-2700 l/m₂.h.bar, while the water absorption capacity of the membrane material was only 5% by weight.

EXAMPLE II

Membranes according to Example I were spun and after removal from the coagulation bath the membranes were treated with a NaOCl solution of 40-4000 ppm for at least 24 hours. After this treatment the membranes were still hydrophilic (i.e. water wettable) and having a water flux of 50-4200 l/m₂.h.bar. The membranes contained a maximum amount of PVP of 0-10% by weight. The water absorption capacity was less than 5% by weight.

EXAMPLE III

A membrane prepared according to Example II was subjected to heat treatment at 150°C for 2-30

hours, after the NaOCl treatment. After this treatment the membranes were no longer wettable by water (hydrophobic). The water flux (after moistening with e.g. ethanol) was 50-4200 l/m₂.h.bar. The water absorption capacity of these membranes was less than 1% by weight.

EXAMPLE IV

A solution was prepared from 20 parts by weight polyethersulphone (Victrix®), 10 parts by weight polyvinyl-pyrrolidone, 5 parts by weight isopropylalcohol in 65 parts by weight N-methyl-pyrrolidone. The thus obtained polymer solution was spun to a capillary membrane by coagulation in a water bath of 20-80°C. After removal from the coagulation bath the membranes were dewatered by a subsequent treatment with ethanol and hexane. After deswelling the membranes were subjected to heat treatment at 150°C for 2-30 hours.

After this treatment the membranes still contained 2-10 parts by weight PVP, based on the total membrane dry weight. The flux of the membranes was 500-5000 l/m₂.h.bar, while the water absorption capacity of the membrane material was only 3% by weight.

EXAMPLE V

Membranes according to Example V were spun and after removal from the coagulation bath the membranes were treated with a sodium hypochlorite solution of 40-4000 ppm during at least 24 hours. After this treatment the membranes were still hydrophilic (capable of being moistened) and having a water flux of 500-7500 l/m₂.h.bar. The membranes contained a maximum amount of PVP of 0-5% by weight. The water absorption capacity was less than 3% by weight.

Claims

1. A process for preparing a microporous membrane, starting from a hydrophobic polymer and a hydrophilic polymer by dissolving these polymers first in a solvent or mixture of solvents and subsequently by coagulating in a coagulation bath removing the membrane so obtained from the coagulation bath and subjecting of said membrane to a heat treatment, characterized in that the membrane prior to the heat treatment is treated with an oxidising agent to leach at least a part of the hydrophilic polymer from the matrix.
2. A process according to claim 1, characterized in that, a sodium hypochlorite solution is used as the oxidising agent.

3. A process according to claim 1 or 2, **characterized** in that, the heat treatment is effected at 150 °C for 2-30 hours.

4. A process according to any of the claims 1-3, **characterized** in that, polyetherimide is used as a hydrophobic polymer and polyvinylpyrrolidone is used as a hydrophilic polymer.

5. A process according to any of the claims 1-4, **characterized** in that, N-methylpyrrolidone is used as a solvent for the polymers.

6. A process according to any of the claims 1-5, **characterized** in that, the hydrophobic polymer / hydrophilic polymer / solvent ratio is 10-35% by weight / 15-35% by weight / 85-30% by weight.

7. A process according to any of the claims 1-6, **characterized** in that, a flat or tubular membrane, on or off a support, or in the form of hollow fibers is prepared.

8. Microporous membranes, flat or tubular or in the form of hollow fibers obtained from the process according to claims 1-7 when the hydrophilic polymer is partly or substantially leached from the matrix.

4. Verfahren nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet**, daß Polyetherimid als hydrophobes Polymer und Polyvinylpyrrolidon als hydrophiles Polymer verwendet wird.

5. Verfahren nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet**, daß N-Methylpyrrolidon als Lösungsmittel für die Polymere verwendet wird.

6. Verfahren nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet**, daß das Verhältnis hydrophobisches Polymer / hydrophiles Polymer / Lösungsmittel 10 bis 35 Gew.% / 15 bis 35 Gew.% / 85 - 30 Gew.% beträgt.

7. Verfahren nach einem der Ansprüche 1 bis 6, **dadurch gekennzeichnet**, daß eine flache oder röhrenförmige Membran mit oder ohne eine Unterstützungseinrichtung oder in Form von hohlen Fasern hergestellt wird.

8. Mikroporöse Membranen, die flach oder röhrenförmig oder in Form von hohlen Faser ausgebildet sind, welche mittels des Verfahrens nach den Ansprüchen 1 bis 7 herstellbar sind, wenn das hydrophile Polymer teilweise oder fast vollständig aus der Matrix ausgewaschen wird.

Patentansprüche

1. Verfahren zum Herstellen einer mikroporösen Membran, ausgehend von einem hydrophoben Polymer und einem hydrophilen Polymer, wobei die Polymere zuerst in einem Lösungsmittel oder einem Gemisch aus Lösungsmitteln aufgelöst werden und anschließend durch Koagulation in einem Koagulationsbad die hierbei erhaltene Membran von dem Koagulationsbad entfernt wird, und wobei die Membran einer Wärmebehandlung unterzogen wird, **dadurch gekennzeichnet**, daß die Membran vor der Wärmebehandlung mit einem oxydierenden Wirkstoff behandelt wird, um wenigstens einen Teil des hydrophilen Polymers aus der Matrix herauszuwaschen.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet**, daß eine Natriumhypochloritlösung als oxydierender Wirkstoff verwendet wird.

3. Verfahren nach Anspruch 1 oder 2, **dadurch gekennzeichnet**, daß die Wärmebehandlung bei einer Temperatur von 150 °C über einen Zeitraum von 2 bis 30 Stunden andauert.

Revendications

35. 1. Procédé de préparation d'une membrane microporeuse, en partant d'un polymère hydrophobe et d'un polymère hydrophile, en dissolvant tout d'abord ces polymères dans un solvant ou mélange de solvants, puis en effectuant une coagulation dans le bain de coagulation, en enlevant la membrane ainsi obtenue du bain de coagulation et en soumettant ladite membrane à un traitement thermique, caractérisé en ce que la membrane, avant le traitement thermique, est traitée avec un agent oxydant pour extraire de la matrice, par lessivage, au moins une partie du polymère hydrophile.

40. 2. Procédé suivant la revendication 1, caractérisé en ce qu'une solution d'hypochlorite de sodium est utilisée comme agent oxydant.

45. 3. Procédé suivant la revendication 1 ou 2, caractérisé en ce que le traitement thermique est effectué à 150 °C pendant 2 à 30 heures.

50. 4. Procédé suivant l'une quelconque des revendications 1 à 3, caractérisé en ce qu'un polyé-

therimide est utilisé comme polymère hydrophobe et une polyvinylpyrrolidone est utilisée comme polymère hydrophile.

5. Procédé suivant l'une quelconque des revendications 1 à 4, caractérisé en ce que de la N-méthylpyrrolidone est utilisée comme solvant pour les polymères. 5

6. Procédé suivant l'une quelconque des revendications 1 à 5, caractérisé en ce que le rapport polymère hydrophobe/polymère hydrophile/solvant est égal à 10-35 % en poids/15-35 % en poids/85-30 % en poids. 10

7. Procédé suivant l'une quelconque des revendications 1 à 6, caractérisé en ce qu'une membrane plate ou tubulaire, sur un support ou en l'absence de support, ou bien sous forme de libres creuses, est préparée. 15 20

8. Membranes microporeuses, plates, tubulaires ou sous forme de libres creuses, obtenues par le procédé suivant les revendications 1 à 7, lorsque le polymère hydrophile est extrait partiellement ou en grande partie de la matrice, par lessivage. 25

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